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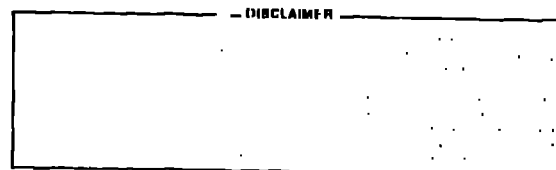TITLE: HIGH TEMPERATURE THERMOCHEMICAL HYDROGEN CYCLES
FOR SOLAR HEAT SOURCES*

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HIGH TEMPERATURE THERMOCHEMICAL HYDROGEN
CYCLES FOR SOLAR HEAT SOURCES

Melvin G. Bowman

I. INTRODUCTION

The utilization of solar thermal systems for the production of fuels is an attractive concept that merits a comprehensive program to achieve economic practicality. It is quite clear, however, that solar concentrator systems will continue to be intermittant heat sources with high capital costs. Consequently, practical utilization of high temperature solar heat will require systems and processes that exhibit high conversion efficiencies and that also incorporate energy storage. Since hydrogen fulfills the requirement for energy storage, is itself an attractive transportable fuel and is the "prime intermediate" in the production of many fuels and chemicals, significant effort should be directed to the development of hydrogen production processes that interface with high temperature solar systems to give efficient heat utilizacion.

The advantages of hydrogen have been widely recognized. Methods for more efficient hydrogen production are the basis for one of the cooperative research and development programs under the International Energy Agency. The electrolysis of water is well known and two of the I.E.A. Annexes are directed toward the development of more efficient and less costly electrolysis processes. One of the Annexes is concerned with improving the electrolysis of acidic and basic solutions at relatively low temperature. The second is concerned with the high temperature electrolysis of steam where stabilized zirconia serves as a solid electrolyte (ref. 1). This material exhibits fair conductivity for oxygen ions and adequately low conductivity for electrons at temperatures of about 1500K. However, efficiencies for electrolytic hydrogen production will be limited by efficiencies for producing electricity and adaptation of existing power production methods to solar heat sources would not be expected to result in high efficiencies. Therefore, the development of high technology processes for efficient D.C. power production (perhaps MHD or thermionic diode systems) may be necessary before electrolysis processes can be coupled to solar heat sources in a realistic way.

One of the important I.E.A. Annexes for hydrogen production is concerned with coupling thermochemical and hybrid thermochemical water splitting cycles to primary heat sources. This I.E.A. activity reflects the wide recognition that thermochemical cycles offer the promise of high efficiency for the utilization of high temperature process heat to decompose water. The potential advantages of such processes have been described several times in glowing terms and literally hundreds of cycles have been conceived and published. For example Bamberger and Richardson have made non-critical tabulations of 201 cycles published up to 1977 (ref. 2 & 3). Of course, many cycles were not included. Unfortunately, many of these cycles are thermochemically invalid and only a few of the well conceived cycles have survived experimental testing and preliminary evaluation. As a result, negative opinions ... thermochemical cycles have been generated and the more recent results based on sound programs are frequently overlooked. Nevertheless, significant progress is being made and this is due in part to the cooperative, information exchange activities within the framework of the I.E.A. It is relevant to note that the development of thermochemical cycles for solar heat sources has been identified recently as one of the areas for cooperation under the I.E.A. agreement on hydrogen production. One important activity will be the re-examination of present processes in terms of their suitability for solar heat sources.

The purpose of this paper is to define some of the criteria required for cycles to couple efficiently with solar heat sources, to examine some of the experimentally validated cycles that have been developed over the years in terms of these criteria and to examine potential cycles that are being considered for the higher temperatures potentially available from solar concentrators.

II. CRITERIA FOR IDEAL CYCLES

One method for defining thermodynamic criteria for efficient cycles, in terms of "ideal" enthalpies and entropies has been presented several times beginning in 1974 (ref. 4). It is presented again here as background for the selection of thermochemical cycles for solar heat sources.

Consider a two-step (single temperature cycle) process in which a reactant (R) reduces water at a low temperature (T_1) to evolve hydrogen and form the compound RO (R may also be an oxide), followed by thermal decomposition of RO at high temperature (T_2) with the evolution of oxygen. The reactions can be written as:

II-1. $R + H_2O \rightarrow RO + H_2$ at T_1

II-2. $RO \rightarrow R + 1/2\ O_2$ at T_2
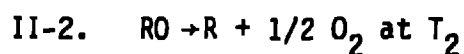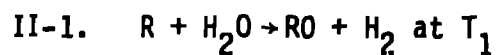
If an ideal cycle is considered to be one in which $\Delta G^O = 0$ for all reactions, and if one utilizes the approximation

$$\Delta G_T^O = \Delta H_{298}^O - T\ \Delta S_{298}^O$$

"ideal" values for entropies and heats of formation (from $R + 1/2\ O_2$) of the compound RO are approximately defined by the expressions:

$$\text{"ideal"}\ \ \Delta S_F^O = \frac{\Delta G_F^O\ (H_2O)\ :\ \text{at}\ T_1}{(T_2 - T_1)}$$

$$\text{"ideal"}\ \ \Delta H_F^O = \Delta S^O \times T_2$$

where $\Delta G^O_F\ (H_2O)$ is the free energy of formation of water at T_1 (the low temperature). To illustrate, if we assume $T_1 = 400$ K (where $\Delta G_f^O(H_2O) = 224$ kJ), and assume different temperatures for T_2, the corresponding parameters computed for RO are those given in Table I.
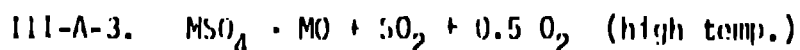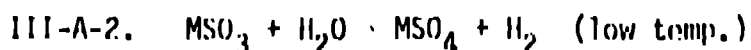
TABLE I

T_2	$-\Delta S_F^O$ (RO)	$-\Delta H_F^O$ (RO)
1200	280 J/K	336 kJ
1500	204	306
2000	140	280
2500	107	268

Since entropies of formation of oxides (per oxygen atom) are character-
istically near -100 J/K, it is clear that very high temperatures will be required
for two-step oxide cycles. This observation is the basis for published statements
that two-step cycles are not feasible. Actually, two-step cycles are possible, in
principle, even for relatively low maximum temperatures if one can identify usable
reactions with the necessary large entropy changes. It should be emphasized that
the entropy changes listed in Table I are minimum absolute values for the indicated
temperatures. Reactions such as II-1, cannot be expected to occur at a reasonable
rate unless the free energy change is negative by a significant amount. Therefore,
the low temperature reaction (or reactions) will be more exothermic than reaction
II-1 and the high temperature reaction or reactions will be more endothermic than
indicated by reaction II-2.

III.   PROCESS DEVELOPMENT OVERVIEW

As indicated above, many of the large numbers of cycles proposed in the
literature are not thermochemically valid. Many of those based on sound thermo-
chemistry have been found to exhibit slow reactions. Thus, it is not surprising
that most of the cycles given serious developmental efforts were not originally
identified by application of the criteria described above. However, the criteria
can be used to determine whether some of the cycles that have been demonstrated
experimentally are suitable for adaptation to solar heat sources. Several of the
cycles described below have been abandoned. Usually, this results from the discovery
of weaknesses in process chemistry. This has also been of value in the development
of thermochemical hydrogen technology by identifying process features that should
be avoided in the selection of cycles.

III-A.   Oxide-Sulfate Cycles. These conceptual cycles were based on attempts
at LASL to use the criteria described above to identify cycles with a minimum number
of reaction steps and maximum temperatures below 1300K. Since ΔS^o values for de-
composition reactions increase with the number of gaseous molecules evolved, our
early studies were directed toward cycles involving the decomposition of sulfates
(ref. 4). The concept can be illustrated by the following equations:

III-A-1. $MO + SO_2 \rightarrow MSO_3$ (low temp.)

III-A-2. $MSO_3 + H_2O \rightarrow MSO_4 + H_2$ (low temp.)

III-A-3. $MSO_4 \rightarrow MO + SO_2 + 0.5\ O_2$ (high temp.)

Typical ΔS^o ~275-290 J/K

Fits ΔT of 800° for two-step H_2O decomposition

As indicated, the typical ΔS^0 for the decomposition of a sulfate to an oxide plus sulfur dioxide and oxygen is sufficiently large for a two-step cycle with a temperature difference of 800^0 between low temperature and high temperature reactions.

It should be noted that reactions III-A-1 and III-A-2 do not represent equilibrium chemistry. For equilibrium at low temperature the sulfite should undergo one of the following reactions.

III-A-4. $\quad MO + SO_2 \rightarrow 0.75\ MSO_4 + 0.25\ MS$

III-A-5. $\quad MO + 1.5\ SO_2 \rightarrow MSO_4 + 0.5\ S$.
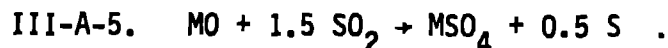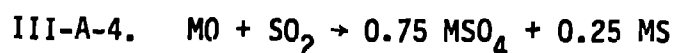
Further, if hydrogen were evolved in reaction III-A-2, it could reduce the metal sulfate according to the equation:

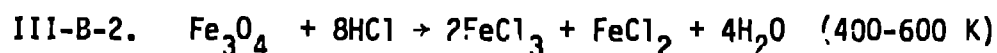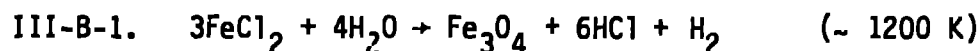III-A-6. $\quad MSO_3 + 3H_2 \rightarrow MS + 3H_2O$.
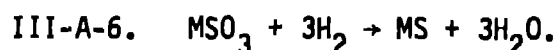
However, most sulfites form and decompose without evidence of the equilibrium reactions. Thus, we were encouraged to attempt to promote reaction III-A-2 in many different sulfate systems representing a wide range of stability. Our results have never included significant hydrogen yields. In most cases, the equilibrium reactions were also not observed.

As a variation of sulfate cycles we also studied cycles based on the formation and decomposition of sulfuric acid (ref. 4.). Several reactions to form sulfuric acid solutions were promoted successfully. Such cycles are currently receiving the major fraction of the worldwide development effort committed to thermochemical hydrogen processes. They will not be described here except to note that the overall decomposition includes a solution concentration step, an evaporation step to form $H_2SO_4(g)$, a decomposition step to form $H_2O(g)$ plus $SO_3(g)$ and the decomposition of SO_3 to form SO_2 plus $0.5\ O_2$. Since homogeneous decomposition reactions occur over significant ranges of temperature, the overall process requires heat over a wide temperature range with the maximum temperature dependent on the pressure of the system. Thus, sulfuric acid cycles are compatible with the heat delivery characteristics of gas-cooled reactors. Indeed they were developed for this type of heat source. However, if sulfuric acid cycles are coupled to solar heat sources, the unique features of such heat sources (higher temperatures and the availability of isothermal heat) will be compromised and potential higher efficiencies will be lost.
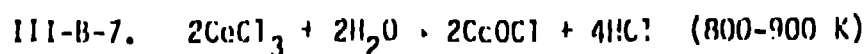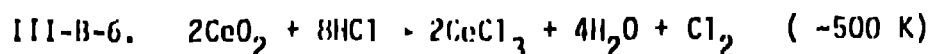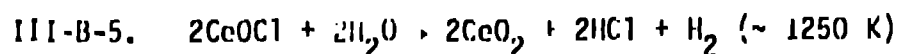
Since solar heat sources are compatible with isothermal, endothermic processes such as the decomposition of a solid, our interest in oxide-sulfate cycles has been renewed. Recent results will be presented below.

III-B. **Halide Hydrolysis Cycles:** For several years most of the process development effort on thermochemical cycles was devoted to the iron chloride cycle. Several different laboratories appeared to claim the origin of the cycle. In recent years, the weaknesses of the cycle have become evident and it is receiving little attention at this time. The effort devoted to the cycle was useful, however, since it identified general features of process chemistry that should be avoided in selecting cycles for practical development. The Institute for Gas Technology version of the cycle (ref. 5) may be described by the following equations.

III-B-1. $3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$ (~ 1200 K)

III-B-2. $Fe_3O_4 + 8HCl \rightarrow 2FeCl_3 + FeCl_2 + 4H_2O$ (400-600 K)

III-B-3. $2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$ (500-700K)

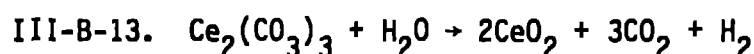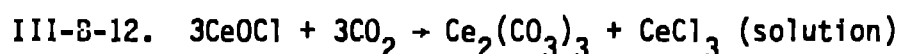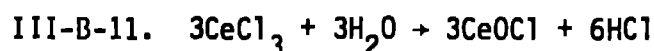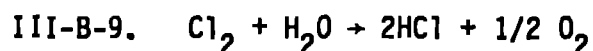III-B-4. $Cl_2 + H_2O \rightarrow 2HCl + 1/2 O_2$ (900-1200 K)

With respect to the criteria described in Section II, the cycle is not attractive. The ΔS for reaction III-B-1 is about 315 J/K. This is larger than the ideal value required for a 1200 K cycle (see Table I), but the yield for the reaction is low which implies that ΔH for the reaction is much larger than the ideal value. In addition, reactions III-B-3 and III-B-4 are endothermic with positive entropy changes. Reaction III-B-3 must be conducted as a cyclic decomposition with low yield in each cycle. Finally, the hydrogen from reaction III-B-1 is mixed with hydrogen chloride and the necessary separation step requires additional expenditure of energy. There is little chance that the cycle will be useful for a solar heat source.

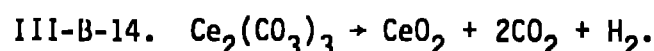An alternate halide-hydrolysis cycle (the cerium chloride cycle) was studied at LASL for a period of time. It may be written as follows.

III-B-5. $2CeOCl + 2H_2O \rightarrow 2CeO_2 + 2HCl + H_2$ (~ 1250 K)

III-B-6. $2CeO_2 + 8HCl \rightarrow 2CeCl_3 + 4H_2O + Cl_2$ (~500 K)

III-B-7. $2CeCl_3 + 2H_2O \rightarrow 2CeOCl + 4HCl$ (800-900 K)

III-B-8. $Cl_2 + H_2O \rightarrow 2HCl + 1/2 O_2$ (900-1000 K)

This cycle does not contain a reaction equivalent to the difficult $FeCl_3$ decomposition (reaction II-B-3) in the iron chloride cycle. However, it includes the remainder of disadvantages cited. Consequently, in an effort to avoid the difficulties associated with reaction III-B-5 , the LASL Cerium-Chloride-Carbonate cycle was conceived. It consists of the following reactions:

III-B-9. $Cl_2 + H_2O \rightarrow 2HCl + 1/2\ O_2$

III-B-10. $2CeO_2 + 8HCl \rightarrow 2CeCl_3 + 4H_2O + Cl_2$

III-B-11. $3CeCl_3 + 3H_2O \rightarrow 3CeOCl + 6HCl$

III-B-12. $3CeOCl + 3CO_2 \rightarrow Ce_2(CO_3)_3 + CeCl_3$ (solution)

III-B-13. $Ce_2(CO_3)_3 + H_2O \rightarrow 2CeO_2 + 3CO_2 + H_2$

or, as an alternate, a dry decomposition,

III-B-14. $Ce_2(CO_3)_3 \rightarrow CeO_2 + 2CO_2 + H_2$.

Good yields have been demonstrated at temperatures below 1000K for all the reactions in the chloride-carbonate cycle. The possibility of splitting either water or carbon dioxide is also an intriguing reality. Nevertheless, the carbonate decomposition reactions (III-B-13 and III-B-14) exhibit entropy changes much greater than the ΔS values indicated in Table I for a 1000K cycle. In addition, reactions III-B-9 and III-B-11 are endothermic with positive ΔS values. Finally, the necessity for the removal of $CeCl_3$ from solution is a very unattractive feature of the cycle.

In retrospect it seems clear that undue effort was devoted to halide cycles. However, the lessons learned with respect to difficult separation and solution drying steps can be valuable in developing the technology base that will be necessary for practical systems. Of course, new halide cycles that incorporate practical solutions to the above problems could still prove to be attractive.

III-C. Alternate Cycles. There are now several thermochemical cycles that have been fully validated by experimental studies. Some of these cycles are based on innovative concepts with unique reactions for the hydrogen and/or oxygen evolution steps. They include cycles from Argonne National Laboratory (ref. 6), Oak Ridge National Laboratory (ref. 7-8), Lawrence Livermore Laboratory (ref. 9) as well as

laboratories in Europe and Japan. Nearly all of the cycles were developed (at least tacitly) for gas cooled reactors as the heat source. Essentially all of the cycles include solution concentration and drying steps. Except for the possibility that low-temperature solar heat might be economic for such drying steps, the cycles as they now exist do not appear to be advantageous for adaptation to solar heat sources.

IV. HIGH TEMPERATURE CYCLES

The high equilibrium temperatures calculated for solar furnaces have prompted several proposals for processes that require temperatures near the computed maximum. It is obvious, of course, that efficiencies for heat utilization at such temperatures will be low because of back radiation from the target. Since hydrogen is of relatively low value, production processes should exhibit high efficiency. Therefore, very high temperature processes must be examined with care before they are assumed to be suitable for solar heat sources.
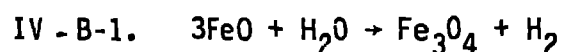
IV-A. Direct Decomposition of H_2O and CO_2

Many proposals have been made for the use of solar heat for the direct decomposition of $H_2O(g)$. Temperatures required for any reasonable yield in the decomposition reaction are certainly at, or higher, than any credible maximum for a practical central receiver facility. Most of the proposals do not recognize the back-radiation problem although ingenious systems for light trapping have also been proposed. Fletcher and Moen have recognized the necessity of separating the H_2 and O_2 at temperature in order to avoid the extremely rapid back reaction as the gases are cooled. They have proposed a separation based on the difference in effusion rates through a ceramic membrane or gauze (ref. 10). However, for temperature limitations imposed by materials properties as well as radiation losses, decomposition yields are low (even for the proposed low pressures) and realistic assessments indicate efficiencies for heat utilization are too low for practicality.

The direct thermal decomposition of CO_2 may be better for a very high temperature process than water decomposition. Certainly, for similar temperatures and pressures, decomposition yields are significantly higher. The dry gases could be quenched to lower temperatures by means of a nozzle expansion without excessive back reaction of CO and O_2. However, in order for this process to be of value, a practical method for separating CO and O_2 at low temperature will be required as well as a practical method for separating H_2 from CO_2 after the shift reaction
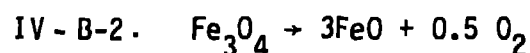
$(CO + H_2O)$ to produce hydrogen. Further, it seems necessary to dry the CO_2 before each high temperature step since traces of H_2O greatly accelerate the $CO + O_2$ back reaction at high temperatures.

IV-B. <u>Oxide Cycles.</u> In considering the problems of interfacing solar heat sources with thermochemical hydrogen processes, it is apparent that a solar furnace can deliver heat at a constant temperature near the temperature maximum. Therefore, cycles involving the high temperature decomposition of a solid (with gas evolution) are entirely feasible. Such "isothermal" steps can lead to better efficiencies (for the same maximum temperature) than steps that interface with the heat delivery characteristics of a gas cooled reactor.

A two-step iron oxide cycle has been proposed several times for use with solar heat. The cycle may be described by the following reactions:

IV-B-1. $\quad 3FeO + H_2O \rightarrow Fe_3O_4 + H_2$

$$\Delta H^o_{(298)}: \text{with } H_2O(\ell) = -19 \text{ kJ}, \Delta S^o = +24 \text{ J/K}$$
$$\text{with } H_2O(g) = -63 \text{ kJ}, \Delta S^o = -95 \text{ J/K}$$

IV-B-2. $\quad Fe_3O_4 \rightarrow 3FeO + 0.5 \ O_2$

$$\Delta H^o_{298} = +305 \text{ kJ}, \Delta S^o = +139 \text{ J/K}$$

Decomposes to $FeO_{(1+x)}$ liquid at ~ 2150 K

Reaction IV-B-1 is a known reaction. It is important to note that reaction IV-B-4 (if written as a solid-solid decomposition reaction), exhibits one of the largest entropy changes known for this type of reaction. At first glance the cycle seems promising, but as one should expect, and as Tofighi, et.al. (ref.11) found, Fe_3O_4 melts before it decomposes and oxygen evolution is over a relatively narrow liquid homogeneity range.

It is unfortunate, perhaps, that Fe_3O_4 melts before it decomposes since suitable substitutes for Fe_3O_4 in this type of cycle have not been identified.

A second type of two-step, oxide cycle includes a solid decomposition reaction to form two gaseous products rather than a condensed phase and gaseous oxygen. The concept can be illustrated by the following equations (where M is a metal),

IV - B-3. $M(s) + H_2O \rightarrow MO + H_2$ (at T_1)

IV - B-4. $MO \rightarrow M(g) + 1/2\ O_2$ (at T_2)
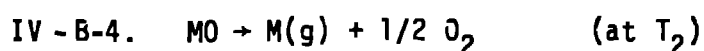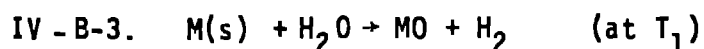
Typical ΔS^o ~200 -210 J/K

If the typical ΔS^o for reactions represented by equation IV - B-4 is compared with values listed in Table I, a temperature difference of ~ 1100° is implied for this cycle. However the high temperature endothermic heat requirement (and the value implied for $\Delta S \times T_2$) includes the sum of the heat of sublimation of the metal plus $-\Delta H^o_f$ (MO). Since entropies of vaporization for metals are fairly similar, the ideal metal for this type of cycle would be one with a low boiling point (to minimize heat of vaporization) that would just reduce water at low temperature. Cadmium and zinc are two candidates frequently mentioned for this type of cycle. Neither is an ideal candidate although both have relatively low boiling points. Published boiling points and oxide decomposition temperatures are as follows:
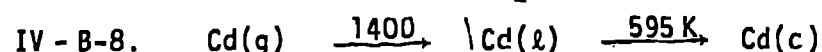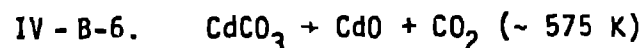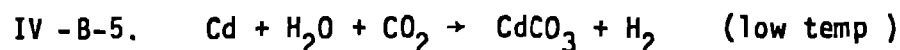
CdO: Td = ~ 1750 - 1850 K, BP (Cd) = 1038 K

ZnO: Td = ~ 2300 K, BP (Zn) = 1180 K

From published thermochemical data, reaction IV - B-3 with Cd should not be expected and, in fact, does not occur. However, in 1976, Pangborn of IGT described an electrochemical method for promoting the reaction (ref. 12). The proposed cycle was not developed into an actual process since projected gas cooled reactors (the "target" heat sources at that time) were not suitable for the high temperature isothermal step, even for the lower CdO decomposition temperatures sometimes reported.

In contrast to the Cd cycle, reaction III - B-3 with Zn is very exothermic. This difference is reflected in the much higher oxide decomposition temperatures. Since back reaction between oxygen and gaseous metal atoms must be minimal, the high decomposition temperature for ZnO implies a very difficult cycle even if the high temperature isothermal heat source is available. Therefore, despite the difficult low temperature reaction, cadmium appears to be the best candidate for this type of cycle.

As mentioned above, Pangborn and co-workers have utilized an electochemical technique to promote the reaction of cadmium with water to form cadmium oxide (via the hydroxide). At LASL, a "pure" thermochemical cycle is under study that incorporates the decomposition of cadmium oxide. It may be described by the following reactions (ref. 13):

IV -B-5. $Cd + H_2O + CO_2 \rightarrow CdCO_3 + H_2$ (low temp)

IV - B-6. $CdCO_3 \rightarrow CdO + CO_2$ (~ 575 K)

IV - B-7. $CdO \rightarrow Cd(g) + 1/2 O_2$ (1600-1800 K)

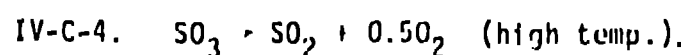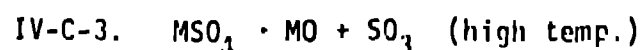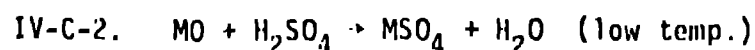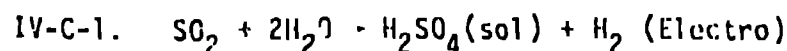IV - B-8. $Cd(g) \xrightarrow{1400} \backslash Cd(\ell) \xrightarrow{595 K} Cd(c)$

the low temperature reaction to form the carbonate does take place, but the yield is limited by the formation of a protective layer of carbonate on the cadmium metal. However, encouraging results have been achieved in reactions where NH_4Cl is used as a catalyst for the reaction. Sufficient heat is available from the condensation of cadmium vapor to promote the carbonate decomposition (reaction IV-B-6).

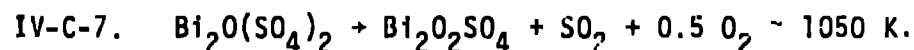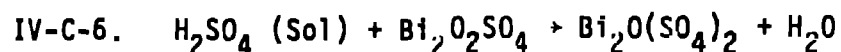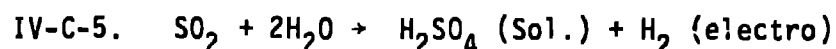The cadmium oxide based cycles offer the potential for high efficiency, if:

(1)   Solar heat can be utilized efficiently for the oxide decomposition step.

(2)   The back reaction between cadmium vapor and oxygen is sufficiently slow.

(3)   The low temperature reactions to yield $Cd(OH)_2$ or $CdCO_3$ can be conducted at practical rates and the resultant solid does not absorb or occlude too much water.

IV-C. Sulfuric Acid - Metal Sulfate Cycles.   As described in Section III-A, unsuccessful attempts have been made to react metal sulfates with water to obtain metal sulfates and hydrogen. As alternates, three different cycles based on an overall sequence of reacting SO_2 with water to produce sulfuric acid and hydrogen have been demonstrated and are under development. However, in addition to rather unsatisfactory methods for achieving the hydrogen evolution step, the cycles involve the formation of sulfuric acid in solution (rather than $H_2SO_4(\ell)$ and require solution concentration and drying operations. Therefore, if the sulfuric acid solution is reacted with a metal oxide to form an insoluble metal sulfate, in principle the sulfuric acid concentration step can be eliminated and corrosion problems can be minimized since the sulfuric acid vapoization step is avoided and the final decomposition involves only the solid and dry gases. The application of the concept to the hybrid sulfuric acid cycle is described by the following equations:

IV-C-1. $SO_2 + 2H_2O \rightarrow H_2SO_4(sol) + H_2$ (Electro)

IV-C-2. $MO + H_2SO_4 \rightarrow MSO_4 + H_2O$ (low temp.)

IV-C-3. $MSO_4 \rightarrow MO + SO_3$ (high temp.)

IV-C-4. $SO_3 \rightarrow SO_2 + 0.5O_2$ (high temp.).

For highest efficiencies, the metal sulfate should be insoluble, should not form a hydrate and should not require excessive heat for its decomposition (i.e., should decompose near the SO_3 decomposition temperature). Since the overall decomposition would be essentially an isothermal step, it would not interface well with an HTGR heat source, but could interface with heat from the blanket of a Fusion Reactor and, of course, would be suitable for a solar heat source.

One potential solid sulfate system being studied at LASL involves the formation and decomposition of bismuth oxysulfate. The <u>overall</u> cycle includes the reactions (ref. 14)

IV-C-5. $SO_2 + 2H_2O \rightarrow H_2SO_4$ (Sol.) $+ H_2$ (electro)

IV-C-6. H_2SO_4 (Sol) $+ Bi_2O_2SO_4 \rightarrow Bi_2O(SO_4)_2 + H_2O$

IV-C-7. $Bi_2O(SO_4)_2 \rightarrow Bi_2O_2SO_4 + SO_2 + 0.5\ O_2 \sim 1050$ K.

Since reaction IV-C-6 requires only relatively dilute sulfuric acid, it is possible that less electrical energy will be required for the electrolysis step (reaction IV-C-5) than is required for the hybrid sulfuric acid process.

Bismuth was chosen initially for the hybrid sulfuric acid-metal sulfate cycle for the reasons cited above and also because it was necessary to choose a specific sulfate (with known properties) for a prototype study. However, bismuth is not an abundant element and is relatively expensive. Therefore, other sulfates might prove to be advantageous, even under conditions where the decomposition requires higher temperature (which means a higher heat requirement) with some reduction in potential efficiency.

Some of the sulfate decomposition reactions that have been considered for hybrid sulfuric acid - solid sulfate cycles are listed in Table II. The overall heat requirement (ΔH^{o}_{298}) for each indicated decomposition reaction is also listed. It should be noted that ΔS^{o} values for the decomposition reactions are quite similar. Hence, a higher ΔH^{o}_{298} value also implies a higher decomposition temperature. However, even if the necessary high temperatures were available from solar heat sources, it is unlikely that the first three decomposition reactions (Ba, Ca, & La) will be suitable for practical cycles (since <u>higher</u> decomposition temperatures mean <u>lower</u> efficiences) even though the sulfates are very insoluble. Of course, if the greater stability of these sulfates could be utilized (in some way) to avoid a sulfuric acid formation step, the resultant processes could be useful for solar heat sources.

SULFATE DECOMPOSITION TO

FORM SO_2 + 1/2 O_2

SOLID PHASES		ΔH^o_{298} (kJ)
1.	$BaSO_4 \rightarrow BaO$	585
2.	$CaSO_4 \rightarrow CaO$	510
3.	1/3 $La_2(SO_4)_3 \rightarrow$ 1/3 La_2O_3	420
4.	$MgSO_4 \rightarrow MgO$	380
5.	$ZnSO_4 \rightarrow ZnO$	334
6.	$CuSO_4 \rightarrow CuO$	318
7.	1/2 $La_2 (SO_4)_3 \rightarrow$ 1/2 $La_2O_2SO_4$	(320 - 340)
8.	$Bi_2O(SO_4)_2 \rightarrow Bi_2O_2SO_4$	270
9.	$CaSO_4 + MoO_3 \rightarrow CaMoO_4$	336
10.	1/3 $La_2(SO_4)_3 + MoO_3 \rightarrow$ 1/3 $La_2(MoO_4)_3$	(290)

The next three decomposition reactions (for Mg, Zn & Cu) involve sulfates that are soluble in dilute sulfuric acid and also form hydrates at temperatures usually considered for the oxide-sulfuric acid reactions. Consequently, we have considered them to be less attractive than our other alternatives. Recently, Krikorian and Hosmer (Ref. 15) have noted that the solubility of zinc sulfate decreases with increasing temperature and have proposed a cycle in which the zinc oxide plus sulfuric acid reaction is conducted in an autoclave at temperatures up to 525 K in order to avoid some of the disadvantages of solution drying.

The next two decomposition reations involve only partial decomposition of a sulfate to form an oxysulfate. Reaction number 8 relates to our current version of the bismuth sulfate cycle. The low value for ΔH^o_{298} is very attractive, of course, and may overshadow the disadvantages for bismuth mentioned above. Reaction number 7 is for the partial decomposition of lanthanum trisulfate. The ΔH^o_{298} value is an estimate based on the reaction temperature reported by Nathans and Wendlandt (Ref. 16). Since the heat requirement (and temperature) for this decomposition approximates the

decompositions of zinc and copper sulfates, and since it is less soluble (at any temperature), lanthanum sulfate may prove to be better than either zinc or copper.

The last two reactions listed in Table II illustrate a concept for utilization of displacement reactions (rather than direct decomposition reactions) for the over-all decomposition of a solid sulfate. As indicated, the heat requirement (and reaction temperature) is significantly lower than the corresponding direct decomposition reaction. Therefore, the concept seems attractive for cycles involving very stable sulfates. It may be reported that very encouraging reaction rates have been achieved for reactions 9 and 10.

REFERENCES

1. W. Doenitz, R. Schmidberger, E. Steinheil and R. Streicher, "Hydrogen Production by High Temperature Electrolysis of Water Vapor," Proceedings of the 2nd World Hydrogen Energy Conference, (Page 403), Zurich, Switzerland, Aug. 21-24, 1978.

2. C. E. Bamberger and D. M. Richardson, "Hydrogen Production from Water by Thermochemical Cycles," Cryogenics 16, 197 (1976).

3. C. E. Bamberger and D. M. Richardson, "Hydrogen Production from Water by Thermochemical Cycles; A 1977 Update." Cryogenics, 18, 170 (1978).

4. M. G. Bowman, "Fundamental Aspects of Systems for the Thermochemical Production of Hydrogen from Water," Proceedings of the First National Topical Meeting on Nuclear Process Heat Applications, American Nuclear Society, Los Alamos, New Mexico October 1-3, 1974. (Los Alamos Scientific Laboratory Report No. LA-5795-C).

5. John Gahimer, Mono Mazumder and Jon Pangborn, "Experimental Demonstration of an Iron Chloride Thermochemical Cycle for Hydrogen Production," Presentation at the Eleventh Intersociety Energy Conversion Engineering Conference, Sept. 12-17, 1976, State Line, Nevada.

6. E. H. Appleman, F. Schreiner and B. M. Abraham, "Experimental Verification of the Mercury-Iodine Thermochemical Cycle for the Production of Hydrogen from Water," Proceedings of the 2nd World Hydrogen Energy Conference (page 851), Zurich, Switzerland, 21-24 August 1978.

7. C. L. Bamberger and D. M. Richardson, "Recent Research on Thermochemical Hydrogen Production at The Oak Ridge National Laboratory," Ibid (Page 763).

8. P. R. Robinson and C. E. Bamberger, "Thermochemical Water Splitting Cycles Based upon Reactions of Cerium-and Alkaline Earth Phosphates," Presentation at the 2nd Miami International Conference on Alternative Energy Sources," Miami Beach, FLA. 10-13 December, 1979.

9. O. H. Krikorian, "The Zn Se Thermochemical Cycle for Hydrogen Production: Chemical and Design Studies," Proceedings of the 2nd World Hydrogen Energy Conference, Op. Cit. (Page 791).

10. E. A. Fletcher and R. L. Moen, Science 197, 1050 (1977).

11. A. Torighi, F. Sibieude, M. Duccarroir, and G. Benezech, Rev. Int. Htes Temp. et Refract., Vol. 15, 7-13 (1978).

12. J. B. Pangborn, Proceedings of the 1st World Hydrogen Energy Conference, Miami Beach (1976), Vol. 1, Paper 7A-59.

13. C. F. V. Mason, J. D. Farr and M. G. Bowman, "The Cadmium Carbonate Cycle for the Thermochemical Production of Hydrogen," Los Alamos Scientific Laboratory Report LA-UR-79-263/ (Sept. 1979).

14. K. E. Cox, W. M. Jones and C. E. Peterson, "The LASL Bismuth Sulfate Cycle - 1979 Update," Los Alamos Scientific Laboratory Report LA-UR-79, (Sept. 1979).

15. O. H. Krikorian and P. K. Hosmer, "Zinc Sulfate Decomposition Studies," Lawrence Livermore Laboratory Report UCRL-83340 (Sept. 1979).

16. M. W. Nathans and W. W. Wendlandt, "The Thermal Decomposition of the Rare-Earth Sulfates," J. Inorg. Nucl. Chem., Vol. 24, 86 - 879 (1962).